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	CLASSIFICATION CONFIDENTIAL **CONFIDENTIAL**		STAT
FDD FILE COPY	CENTRAL INTELLIGENCE AGENCY REPORT		
	INFORMATION FROM		
	FOREIGN DOCUMENTS OR RADIO BROADCASTS CD NO.		

COUNTRY   USSR

SUBJECT   Scientific - Chemicals, catalysts

HOW
PUBLISHED   Monthly periodical

WHERE
PUBLISHED   Moscow/Leningrad

DATE
PUBLISHED   Nov 1950

LANGUAGE   Russian

DATE OF
INFORMATION   1950

DATE DIST. // Jul 1951

NO. OF PAGES   4

SUPPLEMENT TO
REPORT NO.

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THIS IS UNEVALUATED INFORMATION

SOURCE   Zhurnal Obshchey Khimii, Vol XX (LXXXII), No 11, 1950, pp 1981-1998.

CLASSIFICATION OF CATALYSTS IN OXIDATION OF ISO-OCTANE AND ETHYLENE

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/Work on the catalytic oxidation of iso-octane and other standard fuels deserves attention, because oxidation of propellants with the aid of catalysts which are either dispersed or embodied within the walls of the combustion chamber may be assumed to lie within the range of interest of USSR investigators/.

Many investigators have studied the action of admixtures on the catalytic activity of solid substances (1). Interesting results have been obtained from investigations of the effects of admixtures on the catalytic properties of metal films (2). Small quantities of admixtures, captured in the preparation of a catalyst, were able to increase its activity many times, or to promote it (3), while large quantities sharply lowered the activity of the catalyst, or poisoned it.

These two phenomena were usually imagined as being separated by an impassable boundary, and it was thought that their mechanisms were qualitatively different. In particular, the poisoning of the catalyst under the circumstances was thought to arise from the blocking of a part of the active surface by an inactive admixture.

However, S. Z. Roginskiy, classifying both the promoting and poisoning phenomena as modification, suggested that admixtures have a dual effect on the activity of the catalyst. On the basis of experimental work on micropromotion by gases, he attributed both phenomena to a common mechanism, namely, the variation of the kinetic constants of the catalyst. In particular, he suggested that very small quantities of admixtures lower the activation energy of the catalytic process, thus promoting the catalyst, while larger quantities raise the activation energy and produce a poisoning effect.

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On the other hand, as a result of kinetic investigations over a number of years into catalytic reactions of deep oxidation of hydrocarbons over a group of catalysts with spinel structure (compounds of the type $Me \cdot Me_2O_4$ containing in addition the free oxide $Me \cdot O$), the authors arrived at the following relationships:

1. For given conditions the energy of activation in oxidation is greater when the catalyst is more active.

2. In Arrhenius' equation $K = K_0 e^{-E/RT}$ (where K is the reaction = velocity constant which varies with the temperature, K_0 is the coefficient, E is the activation energy of the reaction, R is the gas-law constant, and T is the absolute temperature). K_0 changes sharply and symbatically as E varies.

An investigation of the modifying effect of small admixtures (ranging for the most part up to a maximum of 5% of the weight of the catalyst) on catalytic activity was carried out by determining the kinetic constants E and K_0. Iso-octane was subjected to liquid-phase oxidation over magnesium-chromium ($MgCr_2O_4$ + MgO) and copper-chromium ($CuCr_2O_4$ + CuO) catalysts deposited on asbestos and modified by H_3PO_4, H_3BO_4, $BaSO_4$, $NaSiO_3$, $Ba(NO_3)_2$, and HF admixtures. The magnesium-chromium and copper-chromium catalysts had been found to differ sharply from one another in their activity and in their values of activation energy and the coefficient $K_0(4)$. The specific surface of the magnesium-chromium catalyst was subjected to a preliminary test to determine the effect of different quantities (from 1% to 3%) of the H_3PO_4 admixture on its specific surface, and it was found that the specific surface remained practically the same for different quantities of the admixture.

The modifying effect of a KOH admixture on a V_2O_5 catalyst in the oxidation of iso-octane was also investigated.

From these experiments it was concluded that the action of small concentrations of admixtures on different systems of oxidizing catalysts results in the following:

1. The order of a reaction usually decreases.

2. Within the limits of one order the activation energy and the coefficient K_0 vary symbatically.

3. In the two curves expressing the dependence of E and K_0 on the content of an admixture, a maximum is reached simultaneously.

4. There is a linear dependence between the energy of activation E and the logarithm of the coefficient K_0. The plot of $\ln K_0$ against E runs in a straight line from lower left to upper right; for each admixture, as its concentration is increased, the points which represent the correspondingly modified catalysts on the graph of $\ln K_0$ against E move along the straight line to the right and up, reach the maximum values of E and $\ln K_0$ for this admixture (see 3 above), and then begin to move to the left and down along the same straight line. This dependence has been observed before (5), but up to this time has not been sufficiently clarified.

5. The symbatic variation of E and K_0, acting together, automatically leads, at different temperatures, to an alteration of the relation between the activities of catalysts with different concentrations of admixtures.

6. There is no such well-defined connection between the activity and the concentration of an admixture as is inherent in the usual treatment of the action of admixtures for both homogeneous and inhomogeneous surfaces.

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7. The identical quantity of an admixture can either promote or poison a catalyst in different temperature ranges. This arises from the relation $\ln K = f(1/T)$, derived from the Arrhenius equation, which is different for different concentrations of admixtures. This relationship has been noted in earlier published works (6).

For example, for a given quantity of an admixture the reaction's velocity constant K (which is a measure of the catalytic activity) will be lowered if the absolute temperature T is raised. Within a certain temperature interval the respective curves of $\ln K$ plotted against $1/T$, for a pure catalyst, a catalyst with a given concentration of an admixture, and a catalyst with a different concentration of the same admixture will intersect. At the beginning of the interval the curve for the pure catalyst shows the highest value of $\ln K$, and the curve for the last-mentioned catalyst shows the lowest value of $\ln K$. At the end of the interval, however, the pure catalyst has the lowest value of $\ln K$, while the modified catalyst which was formerly the lowest point has the highest value.

8. The results of the experiments led to a partial revision and correction of the above-mentioned concept of Roginskiy on the mechanism of the dual action of admixtures on the activity of a catalyst. Clearly, the whole series of admixtures not only influences the activation energy, but also simultaneously and symbatically varies the value of the coefficient K_0, leading to a whole series of unique variations of the catalytic activity, e.e., to modification.

9. The phenomenon of modification cannot be explained by the blocking of a homogeneous or inhomogeneous surface, since the blocking of the active regions must lead, under all conditions, to a decrease of the total activity of the catalyst. Nor can these effects be explained by the concept of the formation of definite chemical combinations of the admixture with the catalyst, since modifying admixtures vary the kinetic characteristics of the catalyst continuously and according to a unique law.

10. Strong inorganic acids serve as modifiers of chromium catalysts with excesses of basic oxide. On the other hand, alkaline admixtures are effective modifiers of vanadium pentoxide, which possesses clearly expressed acid properties.

11. In the case of modification one naturally may not expect a simple change of the absolute value of activity, but rather an extensive change in the quality of the surface, leading to complex variations of the individual stages of the catalytic process.

12. Previous conceptions of the catalyst as a substance which lowers the activation energy of the reaction are shown to be untenable.

The kinetics of the oxidation of iso-octane were studied, but in this case, wolfram trioxide was used as the catalyst and it was modified by admixing NaOH. The choice of WO_3 as a catalyst was based on the findings of Yelovich, Zhabrova, Margolis, and Roginskiy (7) that only colored oxides of transitional elements of the periodic system serve as suitable catalysts for the deep oxidation of organic compounds. Wolfram belongs to the sixth subgroup of the periodic system, being therefore a transitional element, and forms a number of colored oxides of different valency. Comparatively few studies have been made of WO_3 as a catalyst for the oxidation of organic compounds, and the information on the subject in literature is of a casual character. In the monograph of Marek and Gan (8), certain patent data on the use of WO_3 for the catalytic oxidation of hydrocarbons are cited. Charlot (9) investigated the oxidation of toluene, naphthalene, xylene, and certain other hydrocarbons over the oxides of several metals, including wolfram. According to his data, WO_3 is much more active than MgO or MoO_3, but less active than NiO. NaOH was added up to 8% of the weight of the original catalyst, but addition of more than 3% of the admixture had a negative effect on the activity. One percent of the NaOH admixture produced the maximum activity.

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The kinetics of the oxidation of ethylene in the gaseous phase over the magnesium-chromium catalyst used before (see above) were investigated after the catalyst had been modified by the admixture of small quantities of $NaSiO_3$.

The following conclusions were reached.

1. The same relationships were observed in the catalytic oxidation of iso-octane over WO_3 when modified by admixture of NaOH as those which were noted when this hydrocarbon was oxidized over magnesium-chromium and copper-chromium catalysts modified by various admixtures (see above), although in this particular case a larger concentration of the catalyst on the asbestos was required because of the lower catalytic activity of WO_3.

2. When ethylene was oxidized over a magnesium-chromium catalyst modified by admixture of Na_2SiO_3, similar modification phenomena were observed as in the case of the oxidation of iso-octane over the same catalyst with the same admixture.

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